Quantum simulation of a triatomic chemical reaction with ultracold atoms on a waveguide

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We study the scaling and coordinate transformation to physically simulate quantum three-body collinear chemical reactions of the type A+BC → AB+C by the motion of single ultracold atoms or a weakly interacting Bose-Einstein condensate on an L-shaped waveguide. As an example we show that the parameters to model the reaction F+HH → H+HF with lithium are at reach with current technology. This mapping provides also an inverse scattering tool to find an unknown potential, and a way to transfer the knowledge on molecular reaction dynamics to design beam splitters for cold atoms with control of the channel outcome and vibrational excitation.

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Introduction. Ultracold atoms and ions are relatively easy to isolate, prepare, manipulate and detect by means of highly controllable operations that preserve their quantum coherence in the time scale of processes of interest. They have thus become natural candidates for performing physical, rather than numerical, simulations in which the effective Hamiltonians governing their dynamics can be made equal to the Hamiltonians of very different, simulated, quantum systems. These simulations are thus based on a formal analogy and may predict the behavior of the simulated system under conditions hard to realize and/or calculate in the original one. The simulating system may also be interesting in its own, beyond the parameters relevant for the simulation, and lead to genuinely new phenomena and applications [1]. This opens exciting perspectives for many-body physics [2], and also for few-body systems.

In this letter we show that this approach can be applied to molecular dynamics and chemical reactivity by studying the analogy between reactive collinear three-body chemical reactions and the motion of a single cold atom, or possibly a weakly interacting condensate, on a potential surface designed by a magnetic or optical waveguide. We put the emphasis on the chemical reaction, but the same procedure may shed light also on non-reactive collisions. What we propose and what is facilitated by ultracold atoms is basically a quantum dynamical version of the rolling ball analogy of chemical reactions with the ball ensemble substituted by a condensate or an ultracold-atom wavepacket, and the mechanical model potential by a magnetic or optical waveguide. Quantum effects are important for state to state (rather than averaged) results as well as for reactions involving a light atom transfer such as hydrogen.

Most chemical reactions occur with steric requirements, i.e., a preferred direction of attack. The collinear configuration for the reaction path corresponds in many "abstraction" reactions involving halogen and alkali atoms to the lowest potential barrier and to the preferred orientation within a narrow cone of acceptance [3]. Moreover collinear reactions may be induced by orienting cold polar molecules with strong electric fields via the second order Stark effect [3]. They are also a standard workbench for testing new calculational methods, examining the range of validity of several approximate theories, and exploring parameter variations over a wide range of values, difficult to implement with full 3D calculations. Accurate quantum calculations involve two mathematical coordinates and are still time consuming and specially troublesome when heavy atoms or high energies are involved. The results of interest are usually the branching ratios among the channels or the distribution of produced molecules among the possible vibrational states.

Simulation Setting. The collinear chemical reaction A+BC → AB+C, corresponds to the collision of an atom A and a nonrotating diatomic molecule BC with the three atoms aligned. We assume that the Born-Oppenheimer approximation holds and separate the fast electronic and the slow nuclear motions. In terms of nuclear masses, positions and momenta in a laboratory frame the nuclear motion is governed by the quantum-mechanical Hamiltonian

$$H=\underbrace{\frac{p_A^2}{2m_A}+\frac{p_B^2}{2m_B}+\frac{p_C^2}{2m_C}}_{\mathcal{T}}+V(x_A,x_B,x_C), \qquad (1)$$

where V is the effective interaction between the three nuclei. The first step is the transformation from the "chemical reaction" variables to the atomic "simulation variables". A second important task is to show that the required parameters for the cold atom experiment are available with current technology.

Mass-weighted coordinate system. Let us introduce the center of mass (CM) coordinate $R_{CM}:=(m_Ax_A+m_Bx_B+m_Cx_C)/M$, where $M:=m_A+m_B+m_C$, and the relative coordinates $q_1:=x_B-x_A$, $q_2:=x_C-x_B$. The corresponding momentum operators are $P_{CM}:=\frac{\hbar}{i}\frac{\partial}{\partial R_{CM}}=p_A+p_B+p_C$, $P_{q_1}:=\frac{\hbar}{i}\frac{\partial}{\partial q_1}=\frac{m_A}{M}P_{CM}-p_A$, and $P_{q_2}:=\frac{\hbar}{i}\frac{\partial}{\partial q_2}=p_C-\frac{m_C}{M}P_{CM}$. The kinetic energy $\mathcal{T}$

is not diagonal in terms of them. To diagonalize $\mathcal{T}$, we use the mass-weighted coordinates [3]

$$\begin{aligned} Q_1 &= (aq_1 + bq_2\cos\beta)/(\sqrt{\widetilde{m}}l), \\ Q_2 &= bq_2\sin\beta/(\sqrt{\widetilde{m}}l), \end{aligned} \tag{2}$$

with mass factors $a = \sqrt{m_A(m_B+m_C)/M}$, $b = \sqrt{m_C(m_B+m_A)/M}$, $\tan\beta = \sqrt{m_BM/(m_Am_C)}$, and scaling parameters $\widetilde{m}$ and l that we can choose freely. The corresponding momentum operators are

$$\begin{aligned} P_{Q_1} &:= \frac{\hbar}{i}\frac{\partial}{\partial Q_1} = \frac{la\sqrt{\widetilde{m}}}{m_B+m_C}\left(-\frac{m_B+m_C}{m_A}p_A + p_B + p_C\right) \\ P_{Q_2} &:= \frac{\hbar}{i}\frac{\partial}{\partial Q_2} = bl\sin\beta\sqrt{\widetilde{m}}\left(\frac{1}{m_C}p_C - \frac{1}{m_B}p_B\right), \end{aligned} \tag{3}$$

and the kinetic energy $\mathcal{T}$ takes the form

$$\mathcal{T} = \frac{1}{2M}P_{CM}^2 + \frac{1}{2\widetilde{m}l^2}\left(P_{Q_1}^2 + P_{Q_1}^2\right),$$

The connection between the simulation variables $\{R_{CM}, Q_1, Q_2\}$ and the chemical reaction variables $\{x_A, x_B, x_C\}$ is given by

$$\begin{aligned} x_A &= R_{CM} - \frac{l\sqrt{\widetilde{m}}}{m_A}Q_1, \\ x_B &= R_{CM} + bl\sqrt{\widetilde{m}}\left(\frac{\cos\beta}{m_C}Q_1 - \frac{\sin\beta}{m_B}Q_2\right), \\ x_C &= R_{CM} + \frac{bl\sqrt{\widetilde{m}}}{m_C}(\cos\beta Q_1 + \sin\beta Q_2). \end{aligned} \tag{4}$$

In the following we ignore the trivial center of mass motion and assume that the potential does only depend on the relative differences between the particle positions. Then the corresponding time-dependent Schrödinger equation associated with the Hamiltonian (1) in the new variables is

$$i\hbar\frac{\partial\Psi}{\partial\tau} = -\frac{\hbar^2}{2\widetilde{m}}\left(\frac{\partial^2}{\partial Q_1^2} + \frac{\partial^2}{\partial Q_2^2}\right)\Psi + V_Q(Q_1,Q_2)\Psi, \tag{5}$$

where we have set $\tau = t/l^2$ and

$$V_Q(Q_1,Q_2) = l^2V_q(q_1,q_2) = l^2V(x_A,x_B,x_C). \tag{6}$$

Equation (5) is the important result for the simulation, and describes 2D quantum motion of a quantum particle of mass $\widetilde{m}$ on the potential V_Q.

Potential energy surface. We now specify the potential surface V_q for the interaction between the three particles of the reaction. This might be an ab initio or, more generally, a semiempirical potential. Here we assume the semiempirical London-Eyring-Polanyi-Sato (LEPS) surface [4–6],

$$V_q(q_1,q_2) = \tag{7}$$
$$\frac{1}{1+\Delta}\left[\sum_{i=1}^{3}U_i - \sqrt{\sum_{i=1}^{3}\alpha_i^2 + -\alpha_1\alpha_2 - \alpha_2\alpha_3 - \alpha_1\alpha_3}\right],$$

where
$U_i = \frac{1}{4}D_i\left[(3+\Delta)e^{-2\beta_i(q_i-q_{i0})} - (2+6\Delta)e^{-\beta_i(q_i-q_{i0})}\right]$,
$\alpha_i = \frac{1}{4}D_i\left[(1+3\Delta)e^{-2\beta_i(q_i-q_{i0})} - (6+2\Delta)e^{-\beta_i(q_i-q_{i0})}\right]$,
and $q_3 = q_1 + q_2$. D_i, β_i and q_{i0} are the dissociation energy, the Morse parameter and the equilibrium distance of the i-th diatomic molecules that we can construct from the three atoms. The adjustable parameter Δ is optimized for each reaction. In the asymptotic regions, before and after the reaction happens, one of the atoms is far from the others and the potential energy is the one of a diatomic molecule [4]. In the LEPS surface, this is given by the Morse function

$$V_j(q_j) = D_j[1 - e^{-\beta_j(q_j-q_{j0})}]^2, \tag{8}$$

where $j = 1$ for the products' channel with the diatomic molecule AB, or $j = 2$ for the reactants' channel with the diatomic molecule BC. This potential near the equilibrium distance q_{j0} can be harmonically approximated by

$$V_j(q_j) = \frac{1}{2}K_j(q_j - q_{j0})^2, \tag{9}$$

where $K_j = 2D_j\beta_j^2$ is the force constant.

Applying Eqs. (4) to the potential in the asymptotic regime where $V_q(q_1,q_2) \approx V_j(q_j)$, we obtain for the simulating frame that the energy surface in the asymptotic regions of the products' and reactants' channels are, taking into account Eq. (6),

$$V_Q(Q_1,Q_2) \approx \frac{1}{2}\widetilde{K}_j\left[\chi_j(Q_1,Q_2) - \chi_{j,0}\right]^2, \tag{10}$$

where we have defined for the products' channel ($j = 1$)

$$\begin{aligned} \chi_{1,0} &= q_{10}\frac{a\sin\beta}{l\sqrt{\widetilde{m}}},\ \widetilde{K}_1 = \frac{K_1\widetilde{m}l^4}{a^2\sin^2\beta}, \\ \chi_1(Q_1,Q_2) &= \sin\beta\,Q_1 - \cos\beta\,Q_2 = \frac{a\sin\beta}{l\sqrt{\widetilde{m}}}q_1, \end{aligned}$$

whereas for the reactants' channel ($j = 2$)

$$\begin{aligned} \chi_{2,0} &= q_{20}\frac{b\sin\beta}{l\sqrt{\widetilde{m}}},\ \widetilde{K}_2 = \frac{K_2\widetilde{m}l^4}{b^2\sin^2\beta}, \\ \chi_2(Q_1,Q_2) &= Q_2 = \frac{b\sin\beta}{l\sqrt{\widetilde{m}}}q_2. \end{aligned}$$

The function χ_1 is a rotation in the (Q_1,Q_2) plane, so the potential Eq. (10) is, for the products, simply a rotated harmonic oscillator in the (Q_1,Q_2) plane. In terms of the oscillation frequencies of the diatomic molecules ν_j, the frequencies $\widetilde{\nu}_j$ of the harmonic oscillators in Eq. (10) are

$$\widetilde{\nu}_1 = \frac{l^2\sqrt{\mu_{AB}}}{a\sin\beta}\nu_1, \quad \widetilde{\nu}_2 = \frac{l^2\sqrt{\mu_{BC}}}{b\sin\beta}\nu_2, \tag{11}$$

where μ_{AB} and μ_{BC} are reduced masses for the diatomic molecules. The value of l can be fixed from these last

equations, so that the potential parameters of the simulation can be made realistic.

Initial atomic velocity. To set the initial velocity of the cold atom v_{Q_1} in the reactants' channel we first estimate the velocities involved in the chemical reaction. If the reaction happens at temperature T the rms mean velocities for the atom A and diatomic molecule BC along a given direction are respectively $(k_BT/m_A)^{1/2}$ and $[k_BT/(m_B+m_C)]^{1/2}$, where k_B is the Boltzmann constant. We may then assume

$$v_C \approx v_B,\ v_A - v_B = \sqrt{k_BT}\left(\frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B+m_C}}\right), \tag{12}$$

which, following from Eqs. (3), corresponds to the atom velocity

$$\begin{aligned} v_{Q_1} &= \frac{la}{\sqrt{\widetilde{m}}}(v_B - v_A) \\ &= al\sqrt{\frac{k_BT}{\widetilde{m}m_A}}\left(1+\sqrt{\frac{m_A}{m_B+m_C}}\right), \qquad (13) \\ v_{Q_2} &\approx 0. \qquad (14) \end{aligned}$$

Example and numerical values. As an explicit example we consider the reaction F+H_2 $\rightarrow$ FH+H, where F$\rightarrow$A, H$\rightarrow$B, and H$\rightarrow$C, so $m_A = 3.15\cdot10^{-26}$ kg and $m_B = m_C = 1.66\cdot10^{-27}$ kg. For this particular reaction, $\Delta = 0.164$ [5], and the mass factors are $a = 5.48\cdot10^{-14}$, $b = 3.98\cdot10^{-14}$ and $\beta = 46.45°$. For the diatomic molecule HF, $q_{10} = 0.917\mathring{A}$, the dissociation energy is $D_1 = 9.609\cdot10^{-19}$ J and the Morse parameter $\beta_1 = 2.242\mathring{A}^{-1}$, so the force constant is $K_1 = 2D_1\beta_1^2 = 966$ N/m. Consequently the oscillation frequency $\nu_1 = (K_1/\mu_{HF})^{1/2}/2\pi = 1.246\cdot10^{14}$ Hz whereas for HH, $q_{20} = 0.742$, $D_2 = 7.608\cdot10^{-19}$ J, $\beta_2 = 1.942\mathring{A}^{-1}$ and $K_2 = 573.85$ N/m so $\nu_2 = (K_2/\mu_{HH})^{1/2}/2\pi = 1.32\cdot10^{14}$ Hz.

To simulate the reaction we propose ^{7}Li atoms. One advantage of ^{7}Li is that the interatomic repulsive interactions are extremely tunable with a Feshbach resonance. The zero crossing of the s-wave scattering length is the shallowest known, so that only modest field stability is needed to achieve a non-interacting gas [7]. We thus have $\widetilde{m} = 1.1526\cdot10^{-26}$ kg and set $l = 6.55\cdot10^{-6}$. Defining the valley depths $\widetilde{V}_j = D_jl^2$ $(j=1,2)$ according to Eq. (6), the parameters in the asymptotic region for the reactants' channel are $\widetilde{\nu}_2 = 5.66$ kHz, and $\widetilde{V}_2 = 2.4\,\mu$K, whereas in the asymptotic region of the products' channel, $\widetilde{\nu}_1 = 5.34$ kHz, and $\widetilde{V}_1 = 3\,\mu$K, The choice of a light atom such as lithium is also dictated by the requirement of achievable transverse frequencies in the reactants' and products' channels with standard techniques (see below). To illustrate the scaling of distances and velocities note that a displacement of $1\mathring{A}$ of the atom F along the reactants' channel corresponds to a displacement of 7.8 μm of the lithium atom according to Eqs. (2). If the reaction occurs at room temperature, $T = 298$ K, Eq. (13) sets for the lithium atom a velocity $v_{Q_1} = 5$ mm/s along the asymptotic region of the reactants' channel. The control of matter waves at such low velocities is at reach [8]. In Fig. 1 we plot the potential energy of the chemical reaction H_2+F $\rightarrow$ HF+H given by Eq. (7) to see the transformations from the chemical reaction parameters $\{q_1, q_2\}$ into the "laboratory" simulation waveguide on which the ^{7}Li atom moves. Note the advanced saddle, and the deeper product's valley, responsible for the exoergicity and the vibrational excitation of the resulting HF molecule.

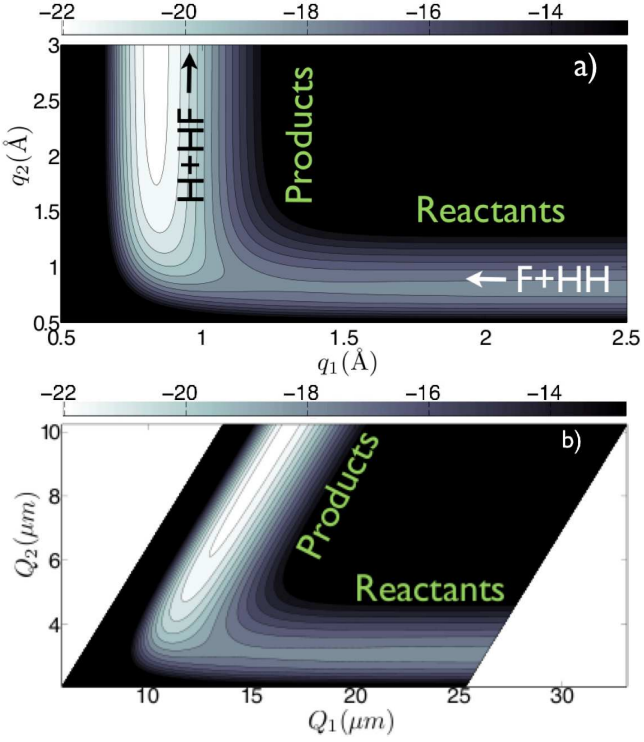

FIG. 1: (Color online) (a) Contour map of the potential energy surface (7) for $H_2 + F \rightarrow HF + H$. (b) Contour map of the potential for the ^{7}Li atom that simulates the chemical reaction. In both cases the energy is in units of the zero point energy of the reactants' valley, and the surface is truncated well below zero energy (the asymptotic value when all atoms are far apart) to better visualize the saddle and reaction path.

The experimental realization with ultracold atoms involves (I) the preparation of a propagating matter wave in a guide and (II) the realization of a guide with the appropriate shape. A Bose-Einstein condensate, rather than the repetition of the experiment with single atoms, provides the ideal setting since the fate of the whole quantum wave packet can be measured in one single experiment. The propagation of a Bose-Einstein condensate into straight magnetic or optical guides has already been demonstrated experimentally [9, 10]. More recently, the production of guided atom lasers shows that a large control of the matter wave parameters such as the mean velocity (5-30 mm/s), the transverse mode occupations, the internal state, or the linear atomic density can be

achieved [11–14]. Using different outcoupling mechanisms, the matter wave can be prepared in the transverse ground state [12, 13]. In these latter schemes, the diluteness of the matter wave suppresses the role of interactions providing a well-suited system for the quantum scattering experiments of interest, without the need of Feshbach resonance tuning. The second aspect deals with the potential modeling to design simple reactive chemical reactions. Different strategies can be envisioned (i) with wires sculptured on atom chips by a focused atom beam technique [15, 16], (ii) with adiabatic radio-frequency potentials [17, 18], (iii) with high resolution time averaged optical potentials "painted" by a tightly focused rapidly moving laser beam on a 2D canvas formed by a static light sheet [19]. A canvas of 60 μm diameter, and a radial condensate thickness of less than 1 μm as the ones realized in [19], are enough for the spatial range and resolution needed for the simulation, see Fig. 1b. Moreover the potential depth can be controlled by velocity or intensity modulation, and no decrease in the number of condensate atoms is observed after 2.5 s, again more than enough for implementing a process of the order of milliseconds. Reaction probabilities could be detected with an *in situ* high resolution imaging, whereas the coherent vibrational excitation is measurable after a few ms time-of-flight. A high flexibility in the guide design is also provided by combining properly these various techniques and/or using time-dependent optical or magnetic potentials [20, 21]. The simplest realization would involve a crossed red-detuned dipole beams configuration in combination with a well positioned repulsive potential wall realized by a sheet of blue-detuned laser light [22]. Alternatively, one could study the motion of an ion into a well-designed guide. Ultracold ions have already been transported in complex structures [23, 24], but their propagation in guides has not been investigated so far.

Discussion and Outlook. We have worked out the mapping between a quantum-mechanical collinear triatomic chemical reaction and the motion of ultracold atoms on a tilted, L-shaped waveguide. As an example we have shown that the parameters for simulating the reaction F + H_2 → FH + H using ^{7}Li can be implemented with currently available technology. This approach is thus complementary to other proposals for simulating chemical reactions [25], which are more ab initio and do not need any previous calculation of the potential surface or application of the Born-Oppenheimer approximation, but require a quantum computation with hundreds of coherently manipulated qubits. This is currently out of reach for a reaction like the one discussed. The present approach is less fundamental, since it assumes a potential surface and the Born-Oppenheimer approximation to hold, but also easier to implement. As an inverse scattering tool, the capability to manipulate the potential parameters may be used to fit experimental results of the chemical reaction and find the right potential.

By a straightforward generalization, we could also simulate collinear four-atom reactions by an ultra-cold atom in a three-dimensional potential. As a further application of the mapping, the vast knowledge and experience accumulated on chemical reaction dynamics, in particular for triatomic systems in the collinear configuration, is now ready to be transferred to design crossed laser beams or waveguide bends with different properties. They could be used, for example, as control devices for asymmetrical beam splitting into the channels or for controlling the transverse vibrational excitation. An example of this is the recent design of an atom diode or one-way barrier [22].

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[1] R. Gerritsma *et al.*, Nature **463**, 68 (2010).
[2] I. Bloch, J. Dalibard, and W. Zwerger, Rev. Mod. Phys. **80**, 885 (2008).
[3] R. D. Levine, Molecular Reaction Dynamics, Cambridge University Press, Cambridge, 2005.
[4] S. Sato, J. Chem. Phys. **23**, 592 (1955).
[5] J. T. Muckerman, J. Chem. Phys. **54**, 1155 (1971).
[6] B. R. Jhonsons and N. W. Winter, J. Chem. Phys. **66**, 4116 (1977).
[7] S. E. Pollack *et al.*, Phys. Rev. Lett. **102**, 090402 (2009).
[8] D. Dries *et al.*, Phys. Rev. A **82**, 033603 (2010).
[9] K. Bongs *et al.*, Phys. Rev. A **63**, 031602 (2001).
[10] A. E. Leanhardt *et al.*, Phys. Rev. Lett. **89**, 040401 (2002).
[11] W. Guerin *et al.*, Phys. Rev. Lett. **97**, 200402 (2006).
[12] A. Couvert *et al.*, Europhys. Lett. **83**, 50001 (2008).
[13] G. L. Gattobigio *et al.*, Phys. Rev. A **80**, 041605(R) (2009) .
[14] G. Kleine Büning *et al.*, Appl. Phys. B **100**, 117 (2010).
[15] J. Reichel, Appl. Phys. B **74**, 469 (2002).
[16] L. Della Pietra *et al.* Phys. Rev. A **75**, 063604 (2007).
[17] O. Morizot *et al.*, Phys. Rev. A **74**, 023617 (2006).
[18] I. Lesanovsky *et al.*, Phys. Rev. A **73**, 033619 (2006)
[19] K. Henderson *et al.*, New J. Phys. **11**, 043030 (2009).
[20] K. W. Madison *et al.*, Phys. Rev. Lett. **84**, 806 (2000).
[21] A. Kaplan *et al.*, Phys. Rev. Lett. **87**, 274101 (2001)
[22] E. Torrontegui *et al.*, Phys. Rev. A **82**, 043420 (2010).
[23] R. B. Blakestad *et al.*, Phys. Rev. Lett. **102**, 153002 (2009).
[24] K. Singer *et al.*, Rev. Mod. Phys. **82**, 2609 (2010).
[25] I. Kassal *et al.*, PNAS **105**, 18681 (2008).